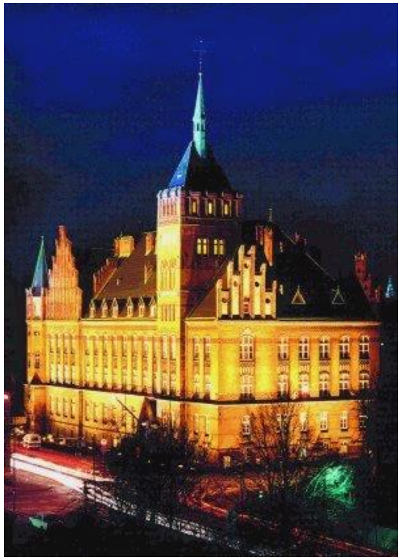


World Congress and Expo on
Recycling

DEPARTMENT OF CHEMICAL ORGANIC TECHOLOGY AND PETROCHEMISTRY
Silesian University of Technology, Poland

Recoverable and recyclable catalysts for sustainable chemical processes

Anna Chrobok

What are the challenges for the sustainable chemical industry today?

- **reduce chemical waste,**
- **improve the selectivity and efficiency of synthetic processes**

The design and synthesis of recoverable and recyclable catalysts

Ludwigshaven in Germany

What are the challenges for the sustainable chemical industry today?

The need to implement ***green chemistry*** principles is a driving force towards the development of recoverable and recyclable catalysts.

Recyclability can either be achieved:

- by bounding the catalyst to a solid phase,
- by modification of solubility characteristics.

CATALYST e.g. acid or base is bounded to a solid phase

Filtration

Regeneration

Recycle

M. Benaglia, *Recoverable and Recyclable Catalysts*, **2009** John Wiley & Sons Ltd., 2009

Green Chemistry

„Green chemistry is the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment.“

(U.S. Environmental Protection Agency)

The 12 Principles of Green Chemistry

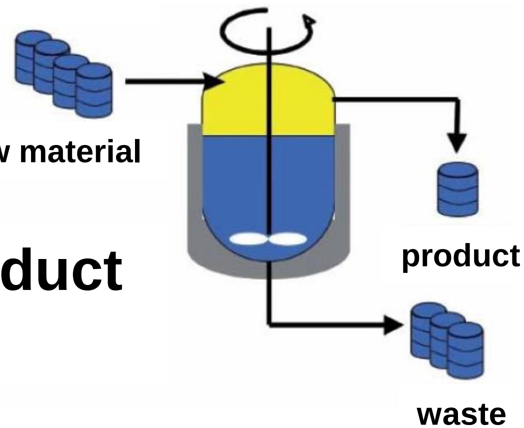
1. Prevent waste
2. Atom Economy
3. Less Hazardous Synthesis
4. Design Benign Chemicals
5. Benign Solvents & Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis (vs. Stoichiometric)
10. Design for Degradation
11. Real-Time Analysis for Pollution Prevention
12. Inherently Benign Chemistry for Accident Prevention

http://www.acs.org/content/acs/en/greenchemistry.html

Green Chemistry

E-factor (kg/kg)

E = kg waste/kg product



Product	tons p.a.	kg waste/ kg product
Oil refining	10^6 - 10^8	ca 0.1
Bulk Chemicals	10^4 - 10^6	< 1 - 5
Fine Chemicals	10^2 - 10^4	5 - 50
Pharmaceuticals	10 - 10^3	25 - 100+

R. A. Sheldon "Consider the Environmental Quotient", *ChemTech*, **1994**, 38.

Examples

Case studies:

the recoverable and recyclable catalysts for chemical processes like:

- esterification,
- Diels-Alder reaction,
- oxidation of alcohols and ketones.

IONIC LIQUIDS as homogeneous and heterogeneous catalysts

Recycling of ionic liquids prevents them from:

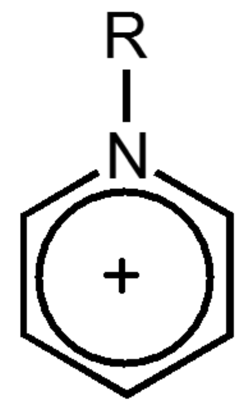
- ending up in the aquatic environment,
- release into the atmosphere (low volatility).

Ionic liquids from **biomass**.

Ionic Liquids Basic Structures

Cations:

$^{+}NR_xH_{4-x}$ $^{+}PR_xH_{4-x}$



Inorganic anions:

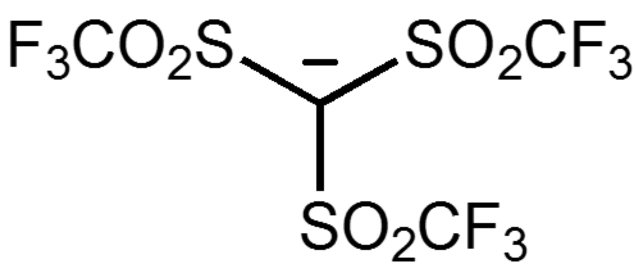
Cl^-, Br^-, I^-, $AlCl_4^-$

BF_4^-, PF_6^-, SbF_6^-

Organic anions:

$(CF_3SO_2)_2N^-$, $CF_3SO_3^-$, $CF_3CO_2^-$

$CH_3SO_3^-$,



Ionic Liquids Properties

rganic an

treme

n sta




Ionic liquids as catalyst and solvent for esterification reaction

Modification of solubility characteristics

Complex hydrogen-bonded anionic clusters

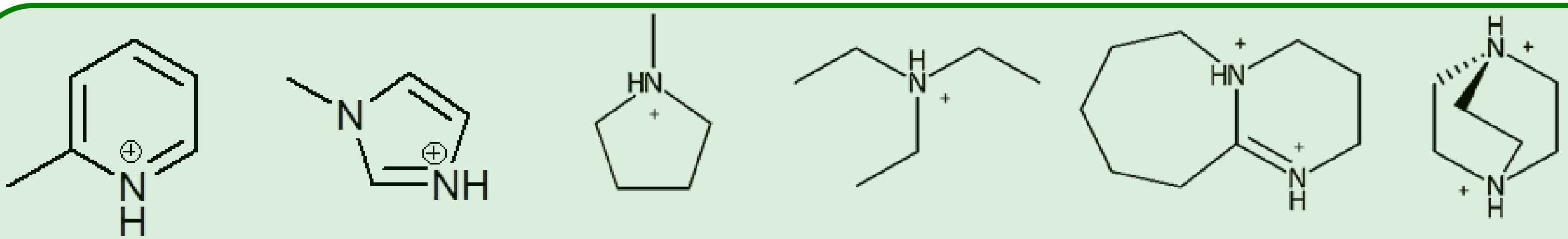
$[(HSO_4)(H_2SO_4)_\chi]^-$ (χ = 0, 1, or 2)

$H_2SO_4 + B \rightarrow [HB][HSO_4]$ **χ_{H2SO4} = 0.50** m. p. < 100°C

$2H_2SO_4 + B \rightarrow [HB][(HSO_4)(H_2SO_4)]$ **χ_{H2SO4} = 0.67**

$3H_2SO_4 + B \rightarrow [HB][(HSO_4)(H_2SO_4)_2]$ **χ_{H2SO4} = 0.75**

(0.67 and 0.75): RT ILs, T_g < 0°C

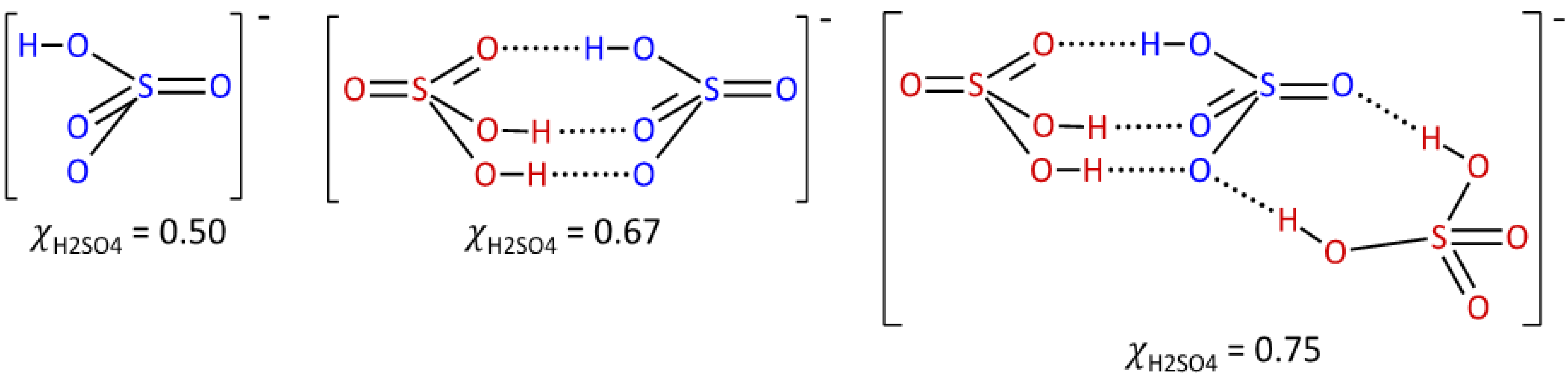


$[H\alpha mpy]^+$	$[Hmim]^+$	$[Hmpyr]^+$	$[Et_3NH]^+$	$[H_2DBU]^{2+}$	$[H_2DABCO]^{2+}$
pK_a = 6.0	pK_a = 6.9	pK_a = 10.5	pK_a = 10.8	pK_a = 13.6	pK_a = 8.8

K. Matuszek, A. Chrobok, F. Coleman, K. R. Seddon, M. Swadźba-Kwaśny, *Green Chem.*, **2014,** 16 , 3463

Complex hydrogen-bonded anionic clusters

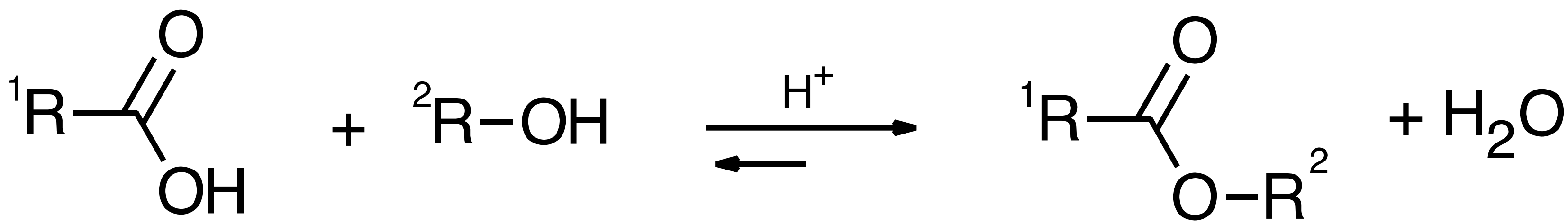
$[(HSO_4)(H_2SO_4)_\chi]^-$ (χ = 0, 1, or 2)



Atoms of the **hydrogensulfate anion** are represented in **blue**,
Atoms of the **sulfuric acid** are in **red**.

K. Matuszek, A. Chrobok, F. Coleman, K. R. Seddon, M. Swadźba-Kwaśny, *Green Chem*., **2014,** 16 , 3463

Model esteryfication reaction

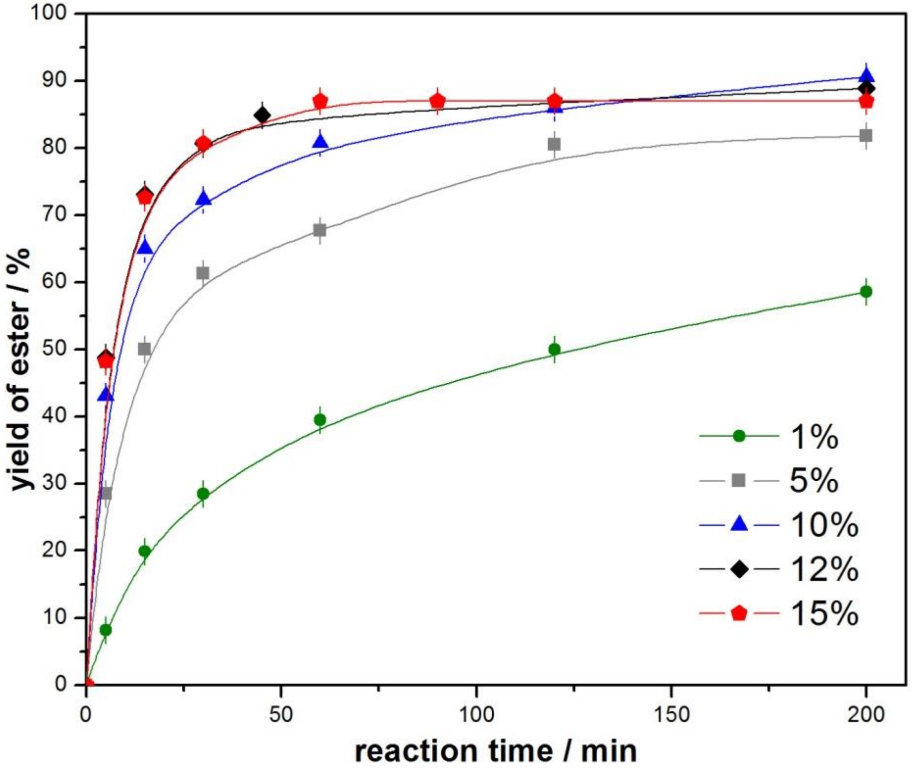


- ✓ Catalyst acidity
- ✓ Reactants ratio 1÷ 1,5 mol
- ✓ Catalyst loading 1÷ 15 % mol
- ✓ Catalyst recycle

K. Matuszek, A. Chrobok, F. Coleman, K. R. Seddon, M. Swadźba-Kwaśny, *Green Chem*., **2014,** 16 *,* 3463

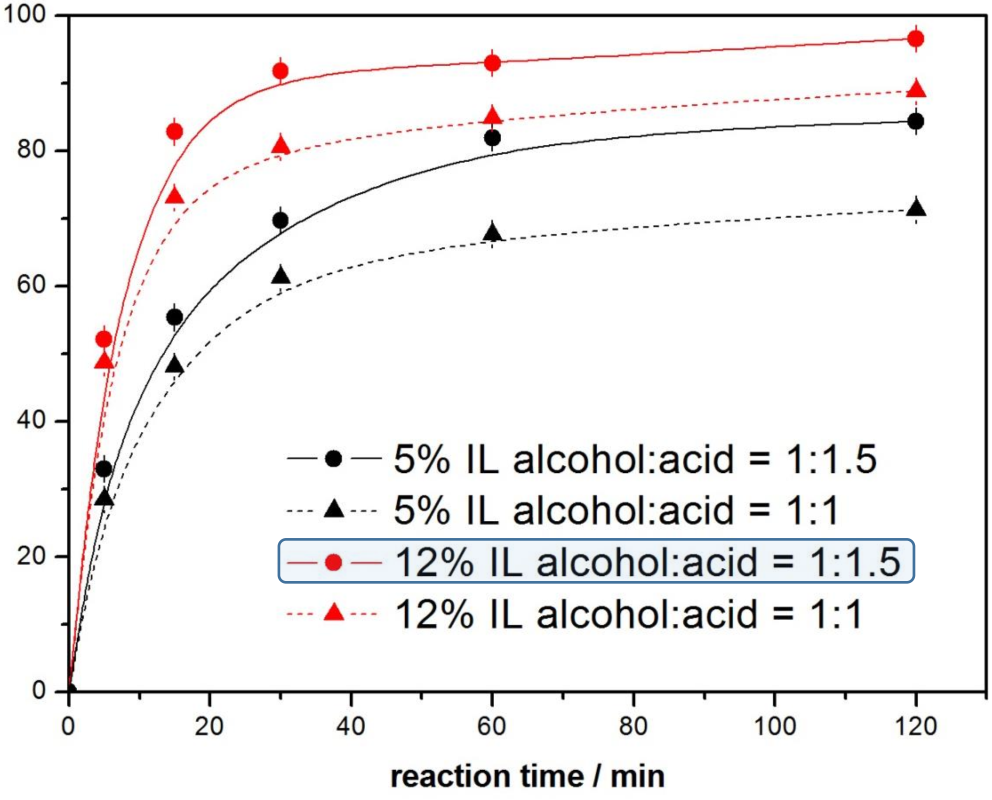
Complex hydrogen-bonded anionic clusters

Catalyst loading, %mol



BuOH : MeCOOH = 1:1; **Temp.** 30^{o}C

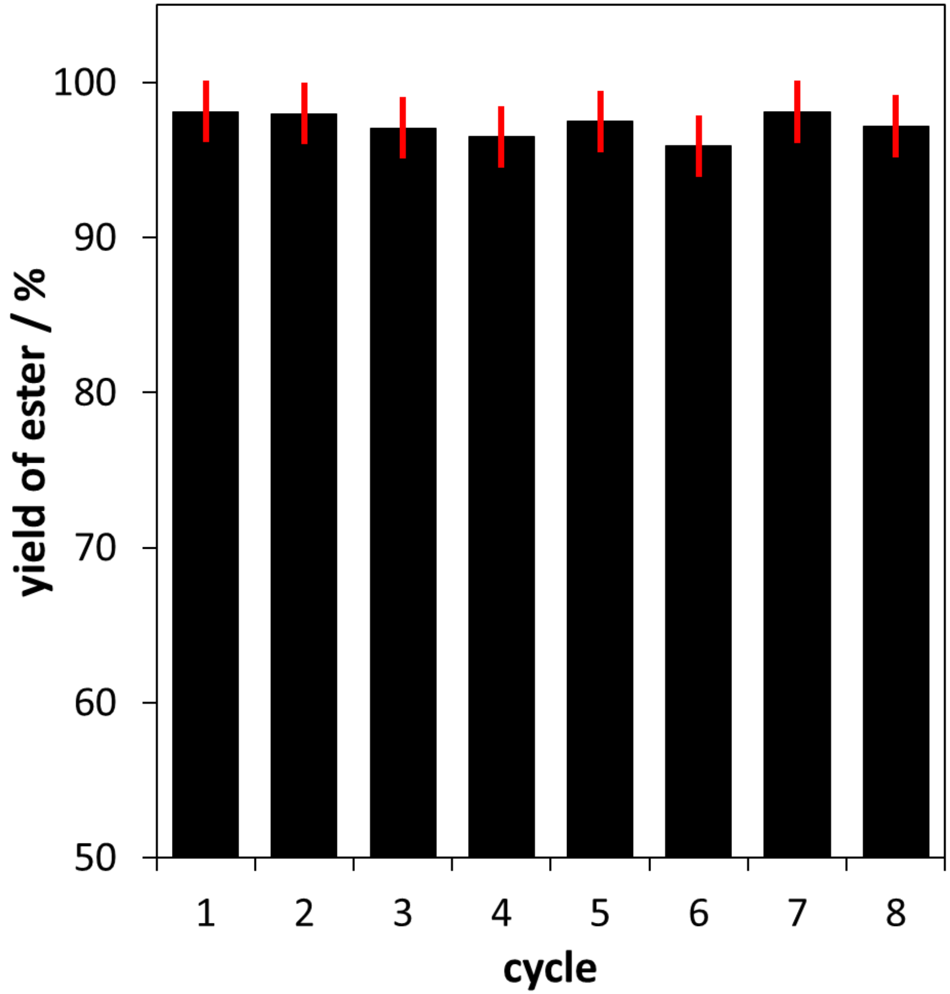
Reactants ratio



Temp. 30^{o}C

$[Et_3NH][(HSO_4)(H_2SO_4)_2]$

Recycling study

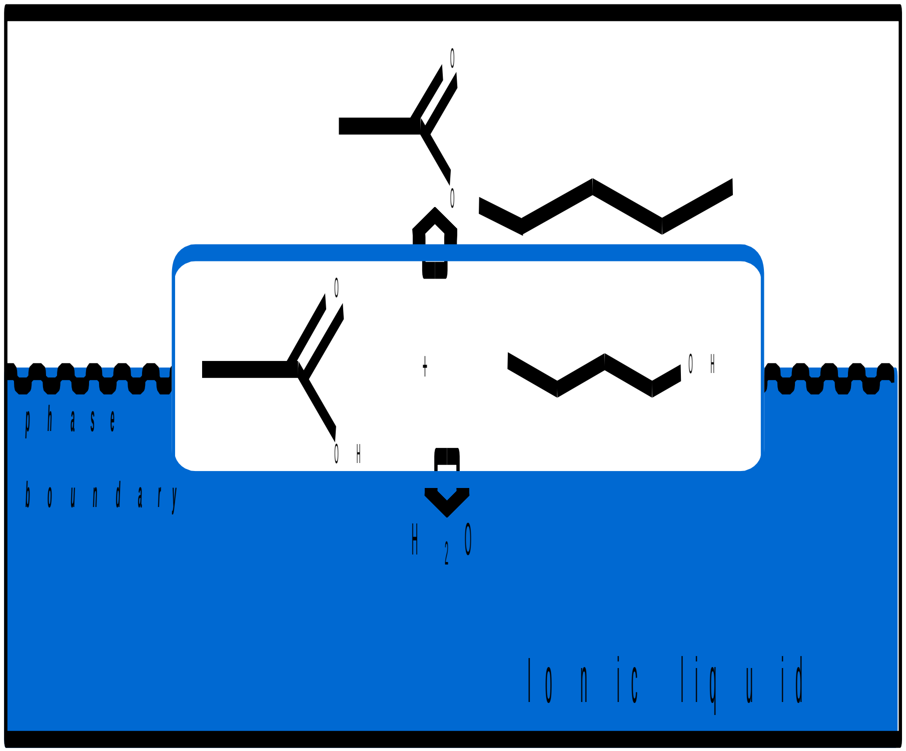


BuOH : MeCOOH = 1:1.5; IL =12% mol; t= 2h; **Temp.** 30^{o}C

[Et_3NH][(HSO_4)(H_2SO_4)$_2$]

Summary

- ✓ Synthesis of a new family of protonic ionic liquids
- ✓ Formation of hydrogen-bonded anionic clusters **$[(HSO_4)(H_2SO_4)_\chi]^-$ (χ= 1 or 2)**
- ✓ High acidity of new ionic liquids (AN up to 121)
- ✓ New catalysts for esterification
- ✓ Key parameters effecting the reaction: **miscibility of reagents**, catalyst acidity
- ✓ Possibility to reuse catalyst without the lost of activity



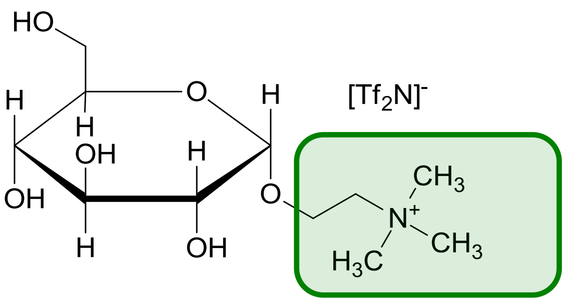



Ionic liquids as catalyst and solvent for Diels-Alder reaction

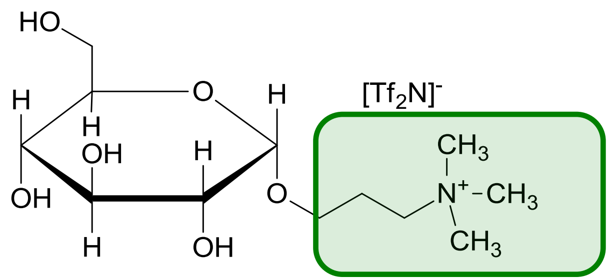
Designing of recyclable biocatalysts

Ionic liquids from the biomass

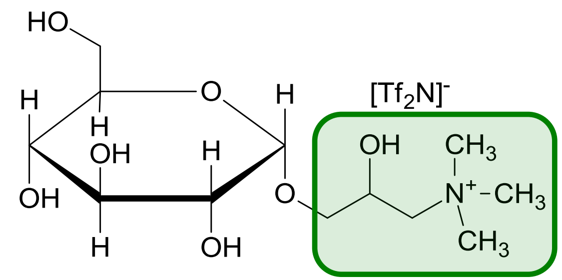
Glucose-derived ionic liquids: exploring biodegradable, low-cost sources



$[GlcO(CH_2)_2N_{111}][Tf_2N]$
(V)



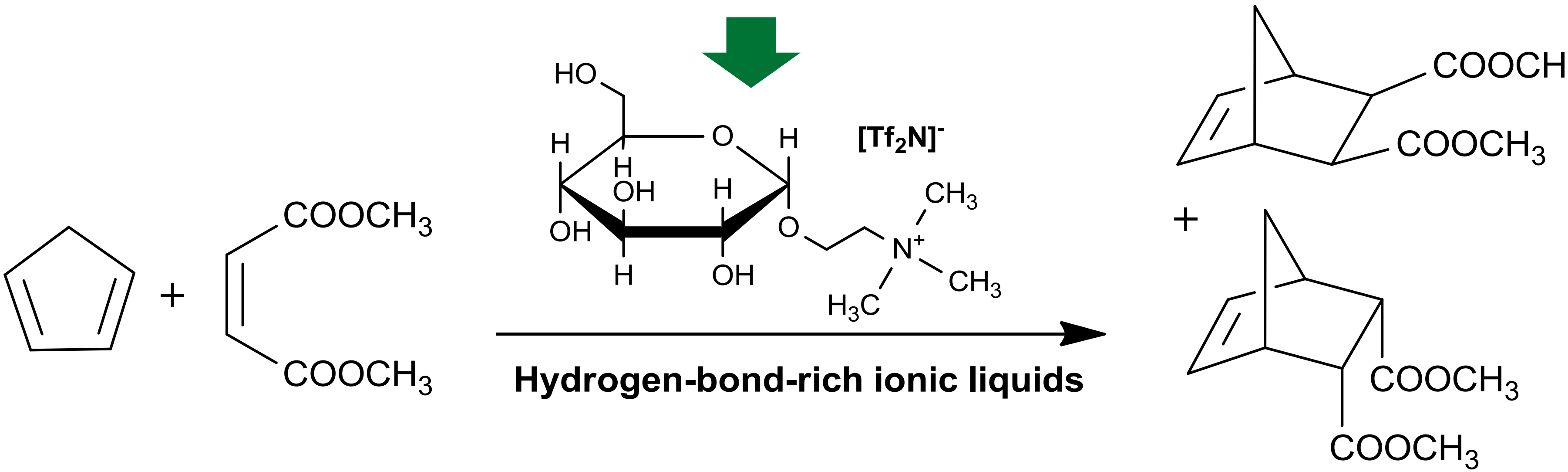
$[GlcO(CH_2)_3N_{111}][Tf_2N]$
(VI)



$[GlcOCH_2CH(OH)CH_2N_{111}][Tf_2N]$
(VII)

K. Erfurt, I. Wandzik, K. Walczak, K. Matuszek, A. Chrobok, *Green Chem*., **2014**, 16, 3508

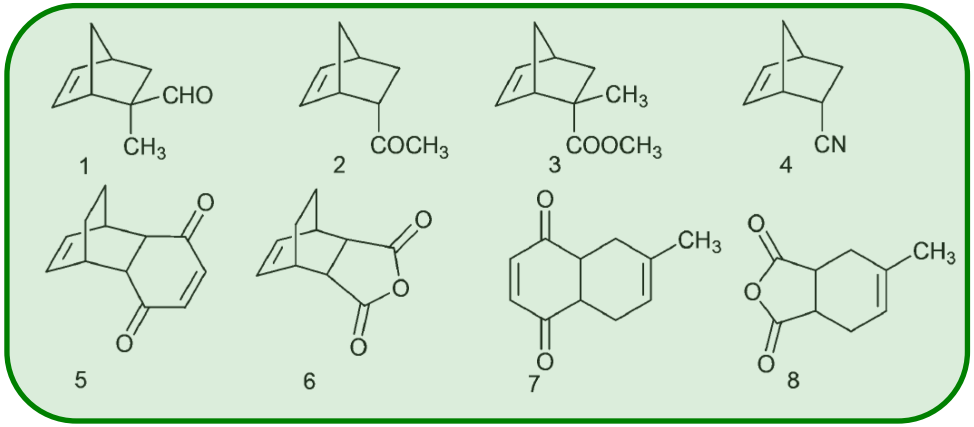
Diels-Alder reaction



K. Erfurt, I. Wandzik, K. Walczak, K. Matuszek, A. Chrobok, *Green Chem*., **2014**, 16, 3508

Diels-Alder reaction

Dienophile	Diene	Product	Time [h]	Yield [%]	*endo: exo*
cyclopentadiene	methacrolein	1	1	96	8.0 : 1
cyclopentadiene	methyl-vinyl ketone	2	10	85	8.2 : 1
cyclopentadiene	methyl methacrylate	3	1	92	1.9 : 1
cyclopentadiene	acrylonitrile	4	1	90	1.8 : 1
cyclohexadiene	1,4-benzoquinone	5	1	96	-
cyclohexadiene	maleic anhydride	6	1	95	-
isoprene	1,4-benzoquinone	7	1	98	-
isoprene	maleic anhydride	8	1	99	-



K. Erfurt, I. Wandzik, K. Walczak, K. Matuszek, A. Chrobok, *Green Chem.*, **2014**, 16, 3508

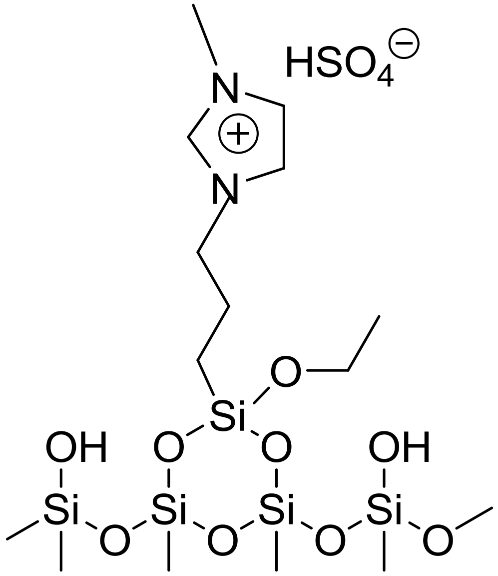


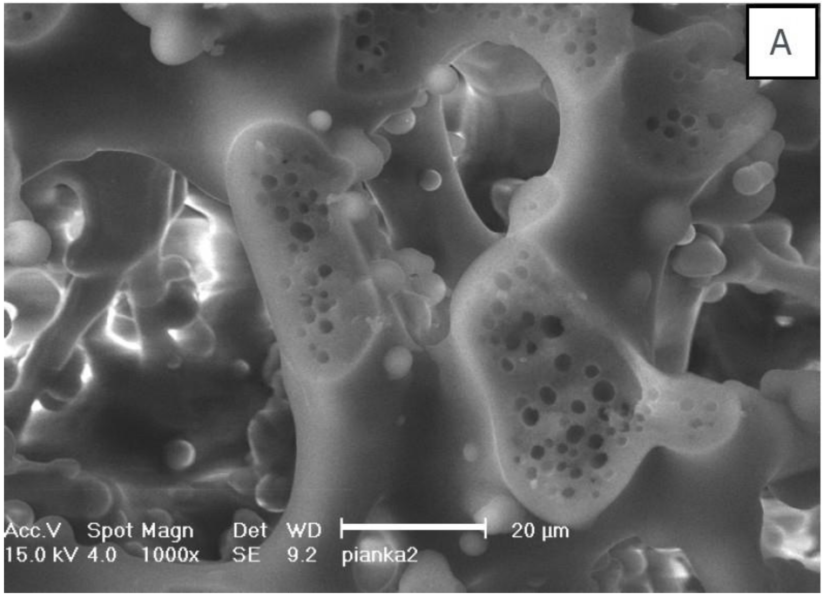

Ionic liquids as catalyst for ketones oxidation

Bounding the catalyst to a solid phase

Immobilized Catalysts

Bounding ionic liquid to a solid phase



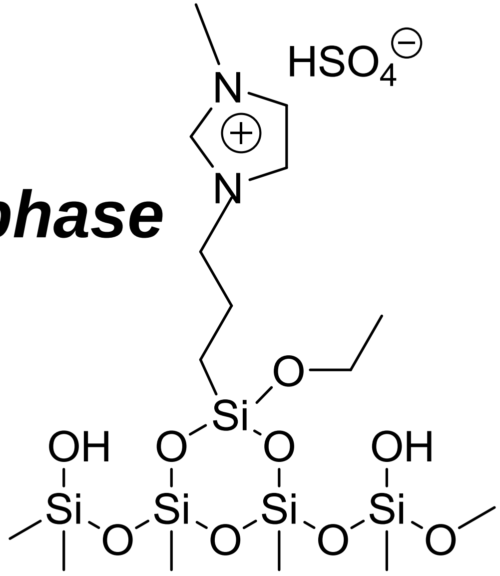


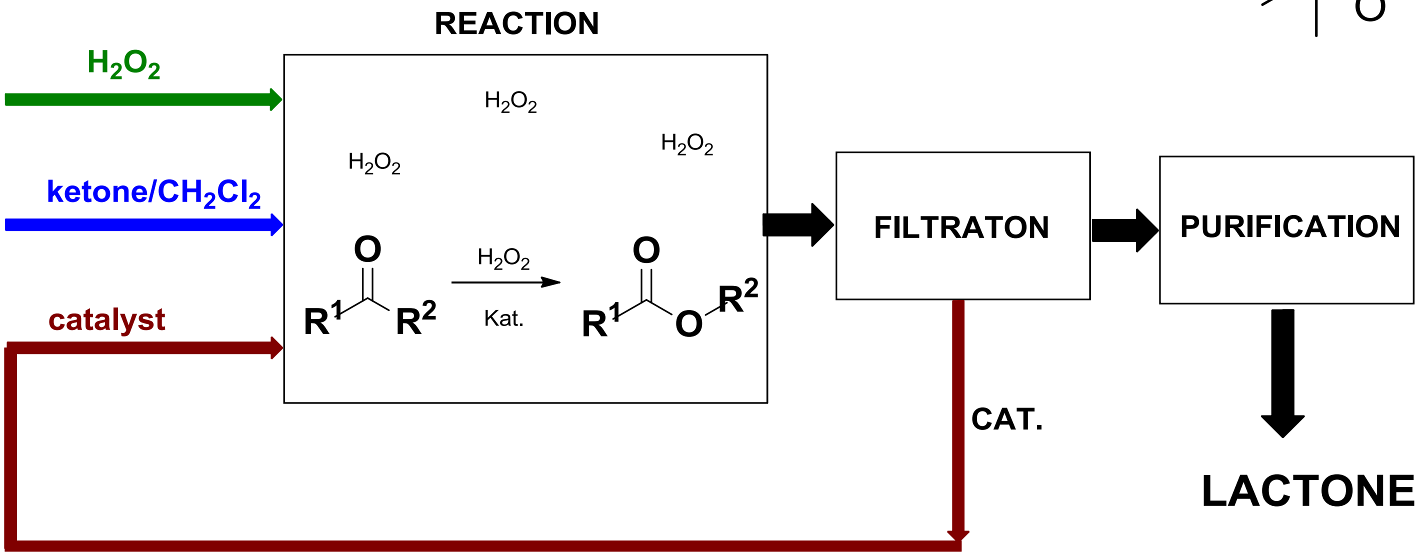
Scanning Electron Microscopy micrograph of bimodal structured silica

A. Chrobok, S. Baj, W. Pudlo, A. Jarzębski, *Appl. Catal. A: General*, **2009,** 366, 22

Immobilized Catalysts

Bounding the catalyst to a solid phase





3 recycles, 89-91% of catalyst recovery

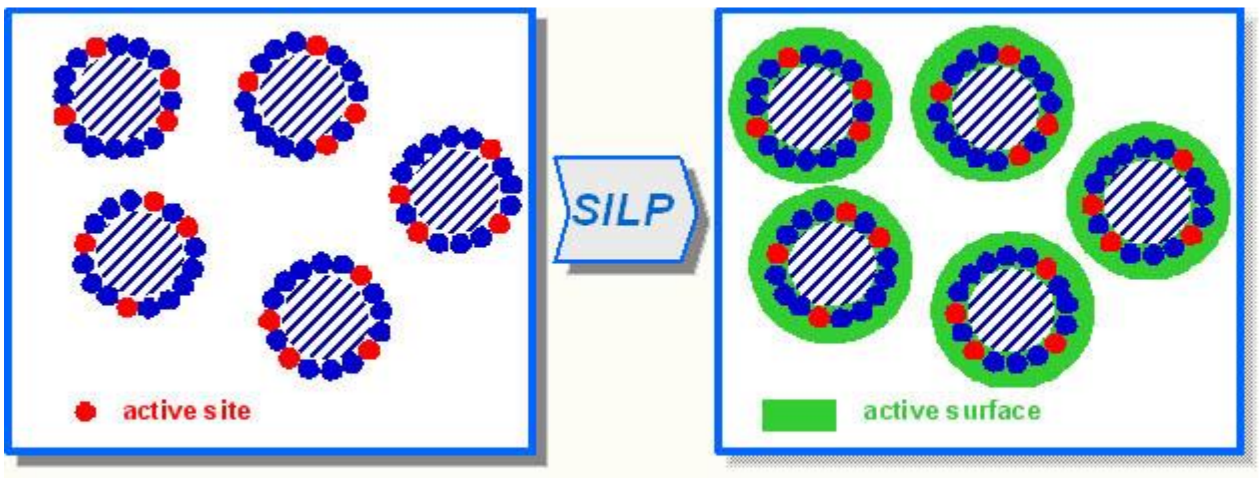
A. Chrobok, S. Baj, W. Pudlo, A. Jarzębski, *Appl. Catal. A: General*, **2009,** 366, 22

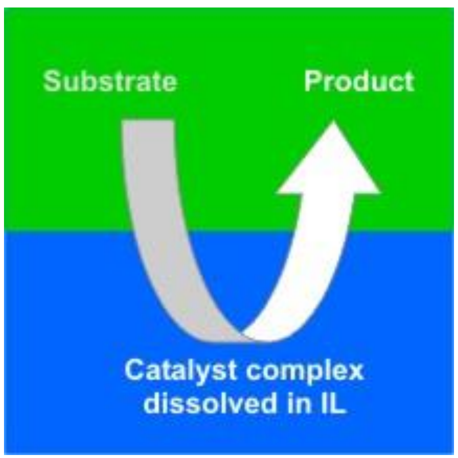
Ionic liquids as catalyst and solvent for alcohols oxidation

Supported Ionic Liquid Phase SILP

Supported Ionic Liquid Phase SILP

- materials science engineering with economic and environmental objectives

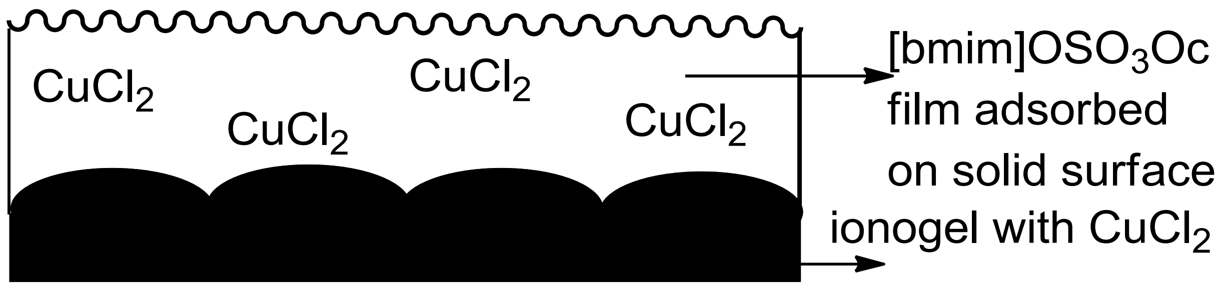


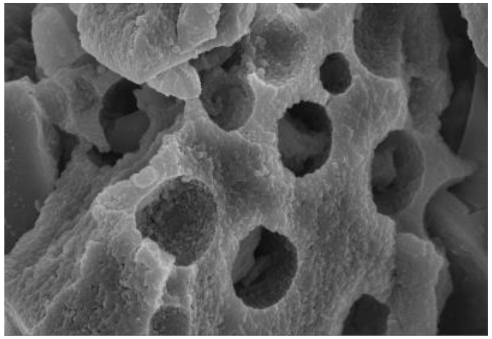


A. Chrobok, S. Baj, W. Pudlo, A. Jarzębski, *Appl. Cat. A: General*, **2010**, 389, 179

Supported Ionic Liquid Phase SILP

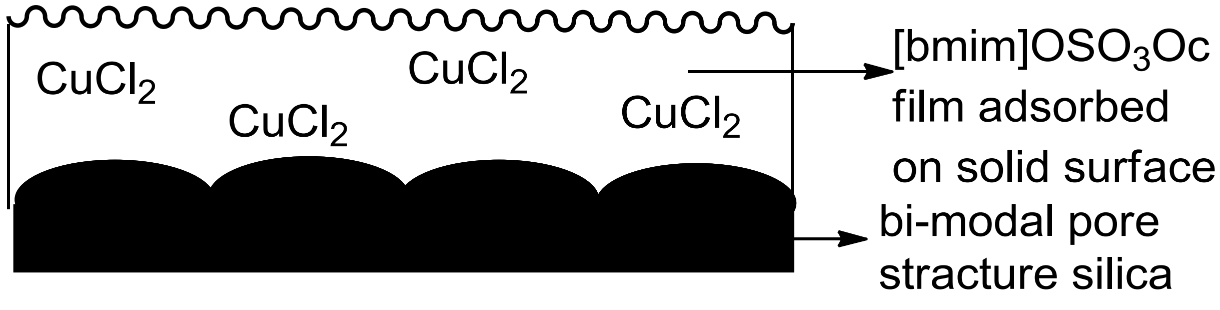
A_$CuCl_2$/[bmim]OSO_3Oc_{sup}





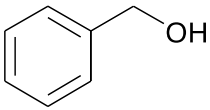
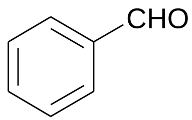
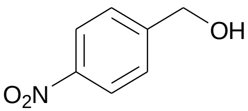
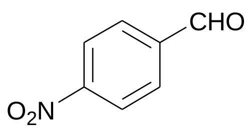
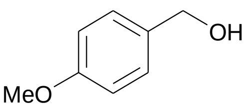
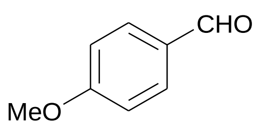
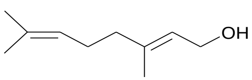
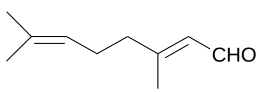
Scanning Electron Microscopy micrograph of the ionogel A_$CuCl_2$/[bmim]OSO_3Oc_{sup}

B_$CuCl_2$/[bmim]OSO_3Oc_{sup}



A. Chrobok, S. Baj, W. Pudlo, A. Jarzębski, *Appl. Cat. A: General*, **2010**, 389, 179

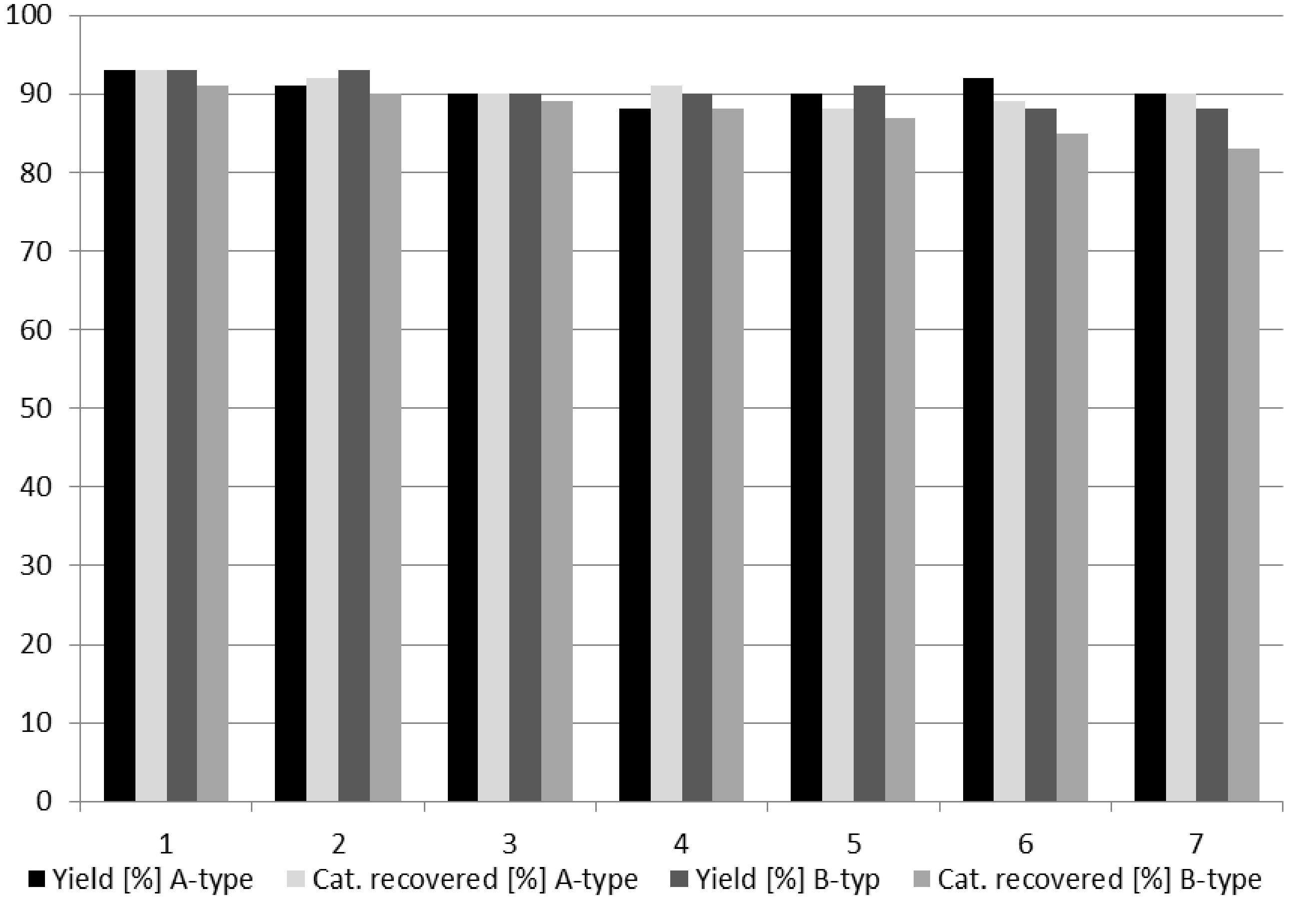
Supported Ionic Liquid Phase SILP

Alcohol	Aldehyde	Time [h]	Conversion[b] [%]	Time [h]	Conversion[b] [%]	Yield[c] [%]	Catalyst recovered [%]
		2	50	7	99	93	93
		2	50	7	99	95	92
		3.5	50	10	99	94	91
		5.5	50	15	99	92	90

reaction conditions: alcohol (1 mmol), TEMPO (0.1 mmol), 0.025 mmol of $CuCl_2$ included in A_$CuCl_2$/[bmim]OSO_3Oc_{sup}, dibutyl ether as solvent, oxygen at atmospheric pressure, 65 ^oC

A. Chrobok, S. Baj, W. Pudlo, A. Jarzębski, *Appl. Cat. A: General*, **2010**, 389, 179

Reusability of the A_$CuCl_2$/[bmim]OSO_3Oc_{sup} and B_$CuCl_2$/[bmim]OSO_3Oc_{sup} catalysts



reaction conditions: benzyl alcohol (5 mmol), TEMPO (0.5 mmol), 0.35g of catalyst containing 0.075 mmol of $CuCl_2$, oxygen at atmospheric pressure, 65 ^{o}C; isolated yields after 7 h with 98% conversion of benzyl alcohol

Summary

The development of **recyclable catalysts** represents a big challenge.

It is interdisciplinary field,
where **pure chemistry** is connected to **material science**, or **engineering** and where even **business and economy-related issues** play an important role in:

- determining the planning, the design and the realization of a project in the area.

It is a field where many technologies and opportunities are offered to successfully realize an easy recoverable and, what is more important, reusable catalytic system.

Acknowledgment

Karolina Matuszek
Agnieszka Drożdż
Magdalena Sitko
Karol Erfurt

Professor Andrzej Jarzębski
Dr Katarzyna Szymańska

Professor Kenneth Seddon
Dr Małgorzata Śwadźba
Dr Fergal Coleman

Financing:

NATIONAL SCIENCE CENTRE
POLAND

HARMONY Grant no. UMO-55 2012/06/M/ST8/00030